Use of an Electrochemical Quartz Crystal Micro Balance (EQCMB) for the Study of Electrochromic Layers

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An Electrochemical Quartz Crystal Micro Balance (EQCMB) is well appropriate to study the intercalation and deintercalation processes of electrochromic layers, because a mass change of about 10^{-9} grams can easily be measured continuously during electrochemical measurements as e.g. cyclic voltammetry (CV) over a large number of cycles and thus the processes at the interface electrolyte/ layer can be analyzed. The interpretation is not always easy, because very often not only an intercalation and deintercalation of cations is observed, but also an adsorption and desorption of anions, a filling of pores of a porous layer as well as the intercalation and deintercalation of e.g. hydrated cations can occur.
The different processes will be explained at the example of a CeO_2-TiO_2-ion storage layer which was deposited on a 5 MHz AT-quartz. The mass of the layer was measured continuously during the first 100 CV cycles in dry ($LiClO_4$ in propylene carbonate) and wet electrolyte (3 wt% water added). An increase of the mass is observed with both electrolytes at the end of each cycle, that is partly due to an irreversible intercalation of Li^+-ions as confirmed by SNMS measurements. In dry electrolyte, a drastic change of the shape of the massograms is observed, that can be explained by simultaneous ClO_4^- desorption and Li^+ intercalation in the cathodic part of the CV and an adsorption of ClO_4^- anions and deintercalation of the Li^+-ions in the anodic part. On the contrary, the shape of the massograms in wet electrolyte is rather constant up to 100 CV cycles, showing an increase of the mass in the cathodic part (Li^+ ion intercalation) and a decrease in the anodic part (Li^+ ion deintercalation). To fit the massograms in wet electrolyte, an intercalation and deintercalation of hydrated Li^+ ions is suggested. The models proposed fit well the massograms recorded in both electrolytes. As time permits EQCMB studies of electrochromic layers (WO_3, NiO-TiO_2) will be also presented.